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PREPARATION OF GLASS CAPILLARY COLUMNS COATED WITH POLAR PHASE FOR HIGH-TEMPERATURE GAS CHROMATOGRAPHY

I. STUDY OF ROUGHENING OF THE GLASS SURFACE

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SUMMARY

Some methods of surface roughening of glass capillary columns have been studied (*viz.*, HCl etching, controlled devitrification and deposition of fine particles).

The reaction of HCl with soda-lime glass proceeds easily, but is a self-limiting process. The resultant NaCl initially forms globules, which become cubic after prolonged heating. The presence of excess of HCl (as in flowing methods) or water reduces the crystallization rate markedly.

A method of surface crystallization based on controlled devitrification has been developed. Spiked surfaces are obtained, which can easily be deactivated by current methods.

The deposition of fine particles on the column wall offers another approach. A method is described for the preparation and application of (sub)micron NaCl particles, which results in a surface comparable with an HCl-etched surface.

Preliminary results are given for surface-roughened capillary columns at high temperatures coated with polar phases.

INTRODUCTION

At present, glass capillary columns offer the best prospects in the analysis of complex biochemical and environmental mixtures. High thermal stability and inertness of the column wall, in addition to a high separation efficiency, are essential for these columns.

During the last 10 years much progress has been made in the development of glass capillary columns[1,2].

It should be acknowledged, however, that current methods of column preparation are inadequate for high-temperature analysis (200–300°), notably for polar phases and trace analyses at the picogram level. The main problems with glass capillary columns in these fields are the catalytic and adsorptive properties (despite its relative inertness), and poor wettability of the glass wall.

The best means of overcoming these problems depend on the polarity of the stationary phase, the sensitivity to be obtained, the column temperature, and the nature of the compounds to be analysed[3–5].

For polar stationary phases, the main problem is caused by poor wetting properties, which are a consequence of their high surface tensions. To promote spreading of these phases, the glass surface must be modified either by an interjacent layer or by roughening. Surface roughening is based on the deposition of a microlayer of fine particles or etching of the glass surface. It provides a convenient and universal approach to wetting promotion, which does not suffer from the limited stability of interjacent layers.

Roughening methods for glass capillary columns

Glass surfaces have been etched with ammonia solution[6,7], sodium hydroxide solution[8,9], hydrofluoric acid[10], and by successive treatments with these solutions[11]. Aqueous methods, however, deeply attack the glass surface[12], and produce strongly adsorbing columns that are useful only in gas–solid chromatography.

Gaseous etching methods are milder. Tesařík and Novotný[13,14] introduced hydrogen chloride and methyl trifluorochloroethyl ether, which splits off HF on heating. Ohline and Jojola[15] had earlier used HF to etch glass beads. The procedure followed by Zhdanov *et al.*[10] may be regarded as the forerunner of gas-phase etching.

Alexander and Rutten[16] prepared polar phase-coated columns for steroid analysis from HCl-etched soda-lime glass capillaries, and in a subsequent paper[17] they described studies on the wetting characteristics of etched glasses. It has been shown that HCl-etched columns can be coated with many stationary phases[18–20] and can be applied in many different fields[21–23]. Etched columns are also useful in the preparation of thick-film capillaries[24] coated with non-polar phases. If coated with a polar phase, these columns show remarkable inertness, but for non-polar phases additional deactivation is necessary[18,20].

An interesting spiked glass surface was reported by Schieke *et al.*[25], who grew silica whiskers on the walls of Pyrex columns. The effect resulted from treatment with methyl trifluorochloroethyl ether at particular concentrations and temperature. The applicability of this type of column, however, is still in the development stage.

Etching not only roughens the glass surface, but also changes the composition of the upper glass layer. A change in surface composition of the glass affects its adsorptive and catalytic properties and may lead to improved inertness of the column wall. Desty[26] proposed the exchange of Na^+ with Li^+ ions, which results in a matt finish and excellent wettability of the glass. The suitability of these surfaces was not indicated.

Fine particles may also be applied directly to the glass wall. Blumer[27] used Silanox 101, a silanized fumed silica, which has been applied successfully in high-temperature analysis of biological samples[28–31]. The properties of Cab-O-Sil (a non-silanized silica) and some diatomaceous supports have been studied by Cramers *et al.*[32] and by Deelder and co-workers[33,34].

Scope of the present work

It has been our intention to prepare glass capillary columns with a high degree of separation, long durability and reproducible retention characteristics by relatively simple and standardized procedures.

Some years ago, our laboratory reported[16,17] the preparation of high-efficiency HCl-etched polar columns with excellent thermal stability (OV-225, SP 2401, FFAP, Dexsil). As we could not reproduce these results, they were considered to be fortuitous rather than the result from a knowledge of the processes involved. Uneven or incomplete etching has repeatedly been observed, as well as condensation of water on cooling after etching, which destroyed the microcrystals of sodium chloride. Imperfectly etched columns yielded poor performance and durability. Examination with scanning electron microscopy (SEM) revealed considerable differences in the distribution, shape and dimensions of the crystals[17,21,35].

To improve this situation we have concentrated on the various factors that influence the etching of soda-lime glass with gaseous hydrogen chloride, in order to establish a set of optimal conditions of pre-treatment, etching time and temperature.

As an alternative for the gaseous HCl etching (surface roughening by NaCl particles), a method was developed to deposite directly a layer of microparticles of NaCl onto the column wall. Within the framework of investigations to produce simple, rugged surface-roughening methods in our laboratory, we developed a method of surface roughening, based on controlled surface devitrification in the presence of a nucleation catalyst.

EXPERIMENTAL

Surface roughening

Gaseous HCl etching of the column wall. Gaseous HCl only attacks soft alkali glass. The composition of the glasses used in this study is given in Table I. The etching is accomplished either by stagnant (static etching) or flowing (dynamic etching), pure and dry HCl, taken from a cylinder (electronic grade, Matheson, Oevel, Belgium).

The set-up, shown schematically in Fig. 1, allows pre-conditioning of the columns at elevated temperatures as well as treatment with HCl at a constant or programmed temperature. To reduce the temperature gradient along the column during the

TABLE I

COMPOSITION OF THE ALKALI GLASSES

A.R. = A.R. glass, Scott-Ruhrglass, Wertheim, G.F.R.; Rö = Röntgen glass 06, Philips, Eindhoven, The Netherlands; B44 = Verre sodocalcique B44, Choisy-le-roi, France.

Component	*Glass*		
	A.R.	*Rö*	*B44*
SiO_2	67	70	70.2
Na_2O	15	17.8	12.6
CaO	7	8.8	6.0
ZnO	7	0.5	
Al_2O_3	2.5	2.3	4.2
Fe_2O_3			
B_2O_3			1.0
MgO			1.9
BaO			3.8
MnO		0.6	
Other elements		Traces	

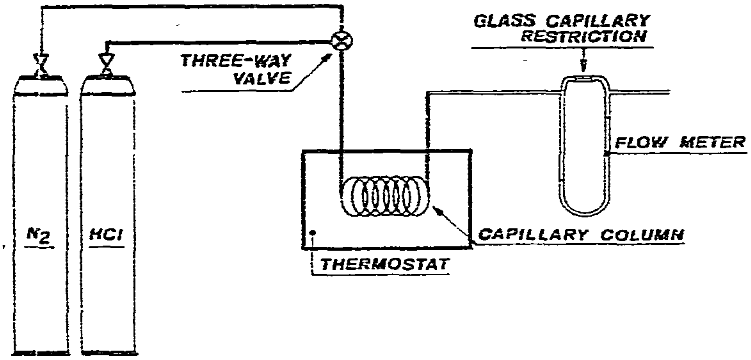


Fig. 1. Schematic set-up for the HCl etching of glass capillary columns.

etching procedure, the columns are wrapped in an aluminium foil in all of the experiments.

The flow is measured continuously with a capillary restriction flow meter, filled with *n*-hexane. Prior to etching all of the columns are dried rigorously by flushing with dry nitrogen at 400° for 16 h at the rate of 40 cm/sec.

After conditioning, the columns involved in the dynamic etching, are cooled to room temperature and the nitrogen flow is replaced with an HCl flow of 20 cm/sec. The column is kept at room temperature for at least 1 h and then heated to the required etching temperature. After etching, the column is flushed again with dry nitrogen, cooled to room temperature and sealed at both ends with a small flame.

For static etching, the columns are likewise pre-conditioned and filled with HCl at room temperature, and sealed at both ends when the HCl concentration exceeds 99.5%. To measure this concentration, a length of about 25 cm is melted off from the column. One end is crushed under water, which rises into the capillary by dissolution of HCl. The filled length is a direct measure of the HCl content in the column.

To study the influence of the etching time at different temperatures, the capillaries are divided in sealed parts of about 6 m, which are consecutively removed from the thermostat at different time intervals. After etching and cooling to room temperature, about 25 cm of each part is melted off to measure the HCl consumption. One end is opened under *n*-hexane which is sucked up into the capillary to an extent equivalent to the HCl consumption. This direct measurement can be used only in the case of static etching. Finally, one end of the remaining part is opened in a dry nitrogen atmosphere and the excess of HCl is forced out by dry nitrogen. Both ends are then sealed.

An indirect measurement of the etching rate, by analysis of the amount and nature of the reaction products, can be performed for both etching methods. The columns were rinsed with about ten times their volume of distilled water and the solutions obtained were analyzed for ionic species by isotachophoresis with an instrument developed by Everaerts *et al.*[36]. The presence of $SiO_2 \cdot nH_2O$ or silicates was assayed for separately by a colorimetric method[37], based on conversion to silicomolybdic acid.

Surface roughening by surface crystallization. A powdered and dried mixture of 75 g of $LiNO_3$, 15 g of KNO_3, 10 g of $NaNO_3$ and 0.5 g of $AgNO_3$ (liquidus 217°) is melted at 240° in a heavy-walled Pyrex container, placed on the bottom of a tall thermostat (1452 D, Packard-Becker, Delft, The Netherlands). The alkali-glass tube (Rö 06, 40 cm × 13 mm O.D. × 6.8 mm I.D.) is placed in the molten salts through a hole in the top cover of the oven. The melt is sucked up gently into the tube until it solidifies in the cold part a few centimetres above the oven cover. The exchange of sodium ions with lithium and silver ions is allowed to take place for 2 h. After melting the plug of solid nitrates with a small flame, the melt runs back into the container. The tube is removed from the oven and, after cooling, is rinsed successively with water and methanol and dried. At this stage, the inner wall of the tube is white and non-transparent. The tube is enclosed in a wide-bore Pyrex tube, which is sealed at both ends after filling with hydrogen and heated at 200° for 20 min. This results in a conversion of Ag^+ ions into colloidal silver and the tube turns brownish yellow. From this tube, capillaries of 0.5 mm I.D. are drawn. The delivery speed was such that a residence time of 30 min in the oven of the glass-drawing machine (about 850°) was obtained.

Deposition of NaCl microparticles on the column wall. A saturated and filtered solution of NaCl in methanol is diluted with 10% of additional methanol. About 8 ml of 1,1,1-trichloroethane is spouted vigorously into 6 ml of this solution. After shaking, a further 8 ml of 1,1,1-trichloroethane are spouted into the sol. This stable and milky sol is then sucked through the column at the rate of 10 cm/sec. The column is provided with buffer columns at both ends in order to ensure a constant speed of the sol in the column. After the sol has left the column, the solvent is evaporated by continuing the suction. Next, the column is treated likewise four more times and then dried. At this stage the column has a faint white appearance. Finally, the NaCl conglomerates are recrystallized at 350° for 1 h.

Scanning electron microscopy

Within half an hour after roughening the capillaries are split open, immediately glued on specimen holders and coated with a gold–carbon layer, so as to avoid the influence of atmospheric water vapour. Kept over silica gel, the specimens were observed to remain unchanged for at least two weeks. Micrographs were taken using a "Stereoscan" (Cambridge Instruments, Cambridge, Great Britain).

RESULTS AND DISCUSSION

HCl etching

Analysis of the reaction products of the etching process showed that Na^+ and Cl^- ions were present in near to equimolar amounts. Ca^{2+} ions were present in trace amounts only, while silicates, $SiO_2 \cdot nH_2O$ and other cations were absent. The amount of NaCl formed in static experiments with a long etching time (26 h), was equivalent to 94% of the amount of HCl consumed. Therefore, this etching method can be described as a dealkalization process in which Na^+ ions in the glass are replaced with H^+ ions. Simultaneously, NaCl is deposited on to the surface as the main reaction product. The vitreous silica network remains intact.

The etching process will be treated as a multiple-step process involving:

(1) formation of NaCl nuclei;

(2) equilibration of the glass surface with gaseous HCl;

(3) diffusion of H^+ ions into the glass in exchange for Na^+ ions;

(4) migration of Na^+ ions across the surface towards NaCl nuclei and particles;

(5) location of Na^+ and Cl^- ions on their respective sites in the NaCl particles, *i.e.*, growth of randomly shaped NaCl particles;

(6) migration of Na^+ and Cl^- ions across the NaCl surface towards low index planes, *i.e.*, recrystallization of NaCl particles.

Under certain conditions, additional processes play a role: formation of extra nuclei during the etching, formation of conglomerates of NaCl particles and growth of large NaCl particles at the cost of smaller ones.

(Ad 1) Formation of NaCl nuclei. SEM pictures of freshly drawn and untreated columns showed a smooth surface carrying no or only a few impurities. SEM pictures of columns filled with HCl and kept at room temperature, revealed the presence of approximately spherical particles (diameter about 0.2 μm) which are uniformly distributed over the surface, *cf.* Fig. 2. Apparently nucleation even takes place at room temperature and is not a rate-determining step in the etching process. Because diffusion coefficients in the bulk of the glass are extremely small at room temperature, this observation can be explained only by the presence of free alkali on the inner wall of the column.

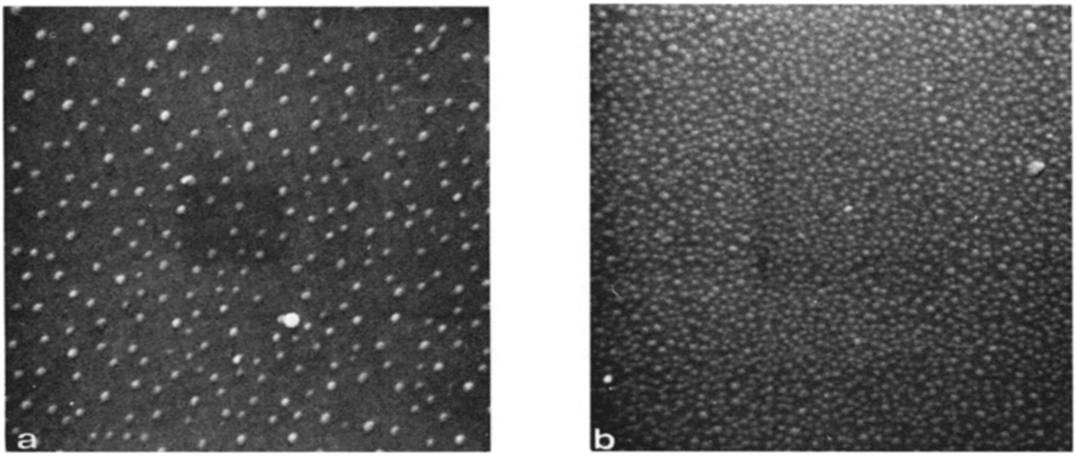


Fig. 2. SEM pictures (10 × 10 μm) of alkali-glass capillaries (A.R.) treated with HCl at room temperature. (a), 1 h; (b), 4 h.

Budd and Kirwan[38] reported surface free alkali on the inner wall of soda-lime silica glass vessels. They found that it was caused by evaporation of the relatively volatile Na_2O from the glass during forming. In glass capillary columns, the vapour-phase Na_2O cannot escape from the column, and on cooling it re-condenses, forming both an alkali-rich surface layer ("skin alkali") and surface free alkali. Nucleation is therefore a consequence of surface impurities rather than of a reaction between HCl and the glass.

(Ad 2–5) Kinetics of the HCl etching. When phase boundary reactions are

fast, the interdiffusion of Na^+ and H^+ in the bulk of the glass is the rate-determining factor. Assuming that the concentration of H^+ ions in the surface layer of the glass is small and proportional to the HCl concentration, the amount of NaCl (M_{NaCl}) formed per unit area in the dynamic etching procedure is given by[39]

$$M_{NaCl} = 2K\,[HCl] \cdot \sqrt{\frac{\tilde{D}t}{\pi}} \tag{1}$$

where

$$K = \frac{[H^+{}_{glass}]}{[HCl]}$$

The functional form of eqn. 1 is preserved even if the interdiffusion coefficient ($\tilde{D}$), describing this binary diffusion process, is a function of concentration[39]. Therefore, M is expected to be proportional to $\sqrt{t}$ no matter what the functional relation between $\tilde{D}$ and concentration may be.

Fig. 3, curve (a), gives the results of a dynamic etching experiment at 350°. The amount of NaCl rapidly approaches a maximum and then remains constant within the limits experimental error (3%). Despite the continuous availability of HCl, the dynamic gaseous HCl etching apparently is a self-limiting process, not follow-

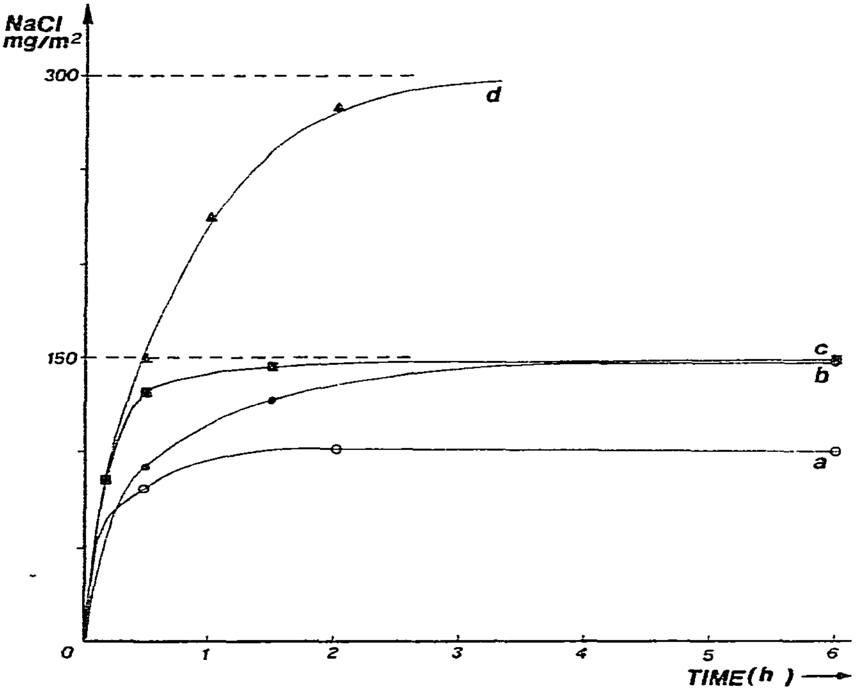
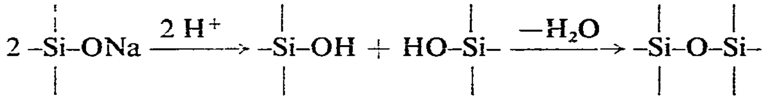


Fig. 3. HCl consumption, expressed as the amount of NaCl formed per square meter of glass surface, at 300° and 350°. Horizontal dashed lines indicate the maximum amount of NaCl that can be formed in 0.25 and 0.5-mm columns with static etching: (a), Dynamic, 350°, I.D. 0.25 mm; (b), static, 300°, I.D. 0.25 mm; (c), static, 350°, I.D. 0.25 mm; (d), static, 350°, I.D. 0.5 mm.

ing eqn. 1. Experiments were performed in which etched columns were rinsed to remove the NaCl and were etched again at 350°. Production of NaCl was observed but at an extremely low rate. Therefore, the limiting factor is connected with the surface layer of the etched glass itself and not with the layer of NaCl. In connection with the concept of skin alkali[38], a mechanism that might cause a sharp decrease in the expected rate of HCl uptake could be a decreasing concentration of alkali with depth into the glass. However, the amount of surface free alkali plus skin alkali, according to Budd and Kirwan, cannot account for the amount of NaCl actually found. This proves that this mechanism is only of marginal importance.

A more satisfactory explanation might be found in the work of Sendt[40] on the dealkalization of soda-lime glasses. He found that the exchange of Na^+ with H^+ is accompanied at and above 350° by a loss of water from the glass, according to the reactions



$$2\,{-}\mathrm{Si}{-}\mathrm{ONa} \xrightarrow{2\,H^+} {-}\mathrm{Si}{-}\mathrm{OH} + \mathrm{HO}{-}\mathrm{Si}{-} \xrightarrow{-H_2O} {-}\mathrm{Si}{-}\mathrm{O}{-}\mathrm{Si}{-}$$

The glass surface layer loses non-bridging oxygen atoms and this loss is expected to reduce the values of both $\tilde{D}$ and K, so that eqn. 1 no longer holds. A surface layer deficient in non-bridging oxygen atoms is known to improve the chemical resistivity of the glass surface[40] and apparently also shields the glass from further attack by HCl.

Curves (b), (c) and (d) in Fig. 3 give the results of a series of static etching experiments at 300° and 350°. It is evident that in static etching of columns up to at least 0.5 mm the limiting factor is the amount of HCl available. For larger diameters shielding is again the limiting factor, as HCl was incompletely consumed in 0.7-mm columns. We reason that in static etching the rate of elimination of water from the glass is reduced by vapour-phase water. Contrary to the dynamic method, in the static method the eliminated water cannot escape from the sealed column. Hence, the development of a shielding layer is retarded, which results in a substantially increased amount of NaCl being formed. Ultimately, elimination of water does occur, which was confirmed experimentally by the condensation of water in colder parts of the columns on rapid cooling, after etching overnight at 350°.

(Ad 4–6) Growth and recrystallization of NaCl particles. The sequence of events occuring during the static etching procedure will be treated with reference to Figs. 2, 4 and 5. At the start of the etching process, exchange of Na^+ with H^+ is fast, partly due to the presence of skin alkali. The Na^+ ions move across the glass surface and randomly locate on the nearest Na^+ site, irrespective of the lattice energy of that particular site. Consequently, the NaCl particles formed tend to have a circular flattened convex shape, and are probably polycrystalline (Fig. 4a). The number of particles is considerably less than the number of nuclei originally present. The surface free energy of small particles is very high, and consequently the smaller nuclei have disappeared in favour of the larger growing particles.

In the course of time, the rate of NaCl formation decreases sharply. Particle growth and recrystallization become competitive effects and the particles tend to have rectangular shapes (Fig. 4b). Ultimately, the development of low index planes becomes predominant (Fig. 4c and d). If the heat treatment is continued for long periods, large NaCl crystals grow at the cost of smaller ones (Fig. 5).

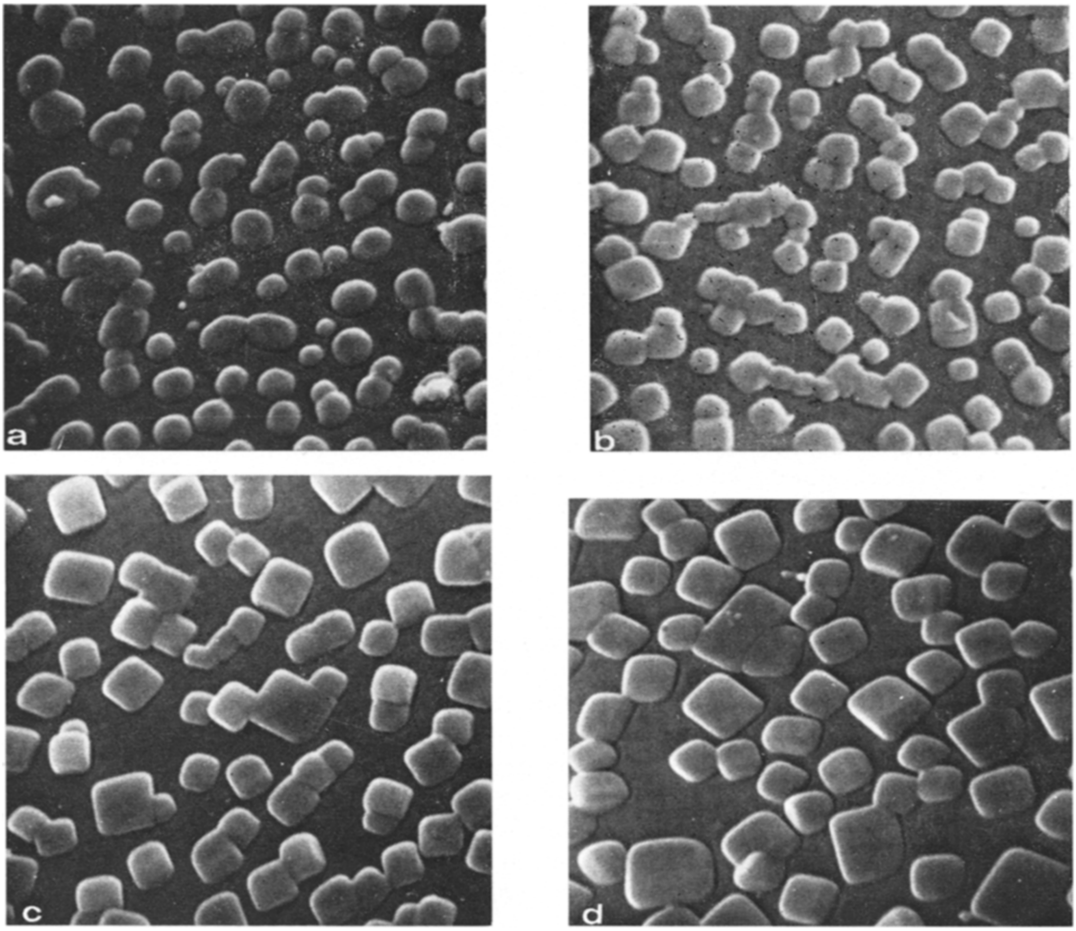


Fig. 4. NaCl particle growth in the course of time for the static procedure at 350°. SEM pictures (10 × 10 μm) of an alkali-glass (A.R.) capillary (I.D. 0.4 mm). (a), 30 min; (b), 60 min; (c), 120 min; (d), 240 min.

During the dynamic etching procedure, HCl is present in excess, which has a marked influence on the rate of particle growth and recrystallization (Fig. 6). The smaller nuclei disappear to a lesser extent than in the static etching. Hence, a large number of relatively small particles is observed. The excess of HCl even induces the formation of additional nuclei on bare parts of the surface (Fig. 6b). The result is that particles of dissimilar size and shape are present, even after 6 h of treatment. Recrystallization apparently is effectively inhibited by the excess of HCl. The number of rectangular particles after 6 h is still negligibly small.

Influence of the etching temperature. The description of the etching process given above relates to an etching temperature of 350°. At 300°, the sequence of events is essentially the same, but slower. At 400°, using A.R. glass, the results are variable. At the start of the etching in some parts of the column, the attack of the glass by HCl is confined to circular areas, randomly distributed over the surface. Consequently,

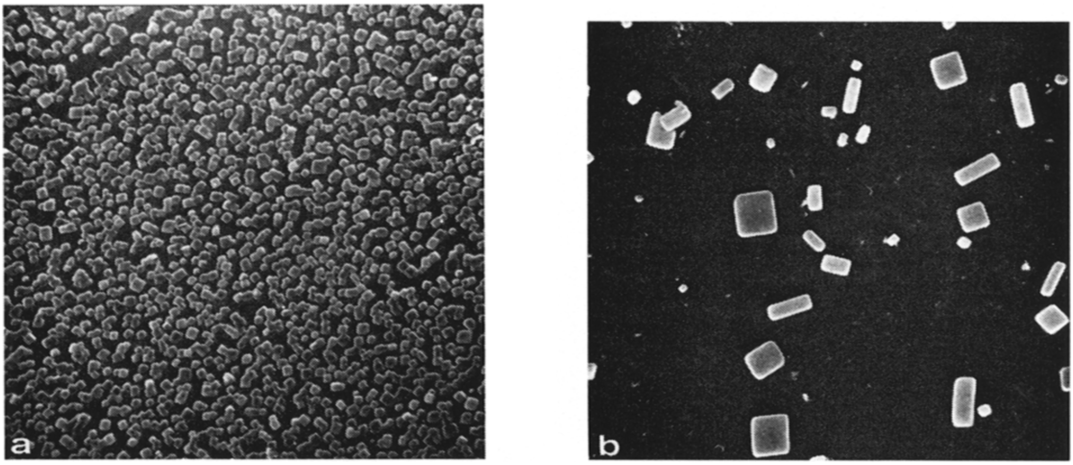


Fig. 5. NaCl particle growth in the course of time for the static procedure at 350°. SEM pictures (50 × 50 μm) of an alkali-glass (A.R.) capillary (*cf.* Fig. 4). (a), 2 h; (b), 22 h.

the distribution of NaCl is not uniform, nor is the rate of recrystallization. The final result is a column locally covered with particles of dissimilar size (up to more than 10 μm), which is far beyond those observed at 350°. This deviation of the "normal" process takes place over about 30% of the column area, the remaining 70% showing a distribution of NaCl as in Figs. 4–6. Therefore, we consider 350° to be the optimal etching temperature.

The rôle of the pre-conditioning. As described under Experimental, the freshly drawn columns are sealed at both ends immediately after drawing. Prior to etching, the columns are rigorously dried by flushing with dry nitrogen at 400°. The intention of these measures is to prevent the formation of a hydrated surface layer or to dehydrate such a layer. If these precautions are omitted, the surface free alkali deliquesces

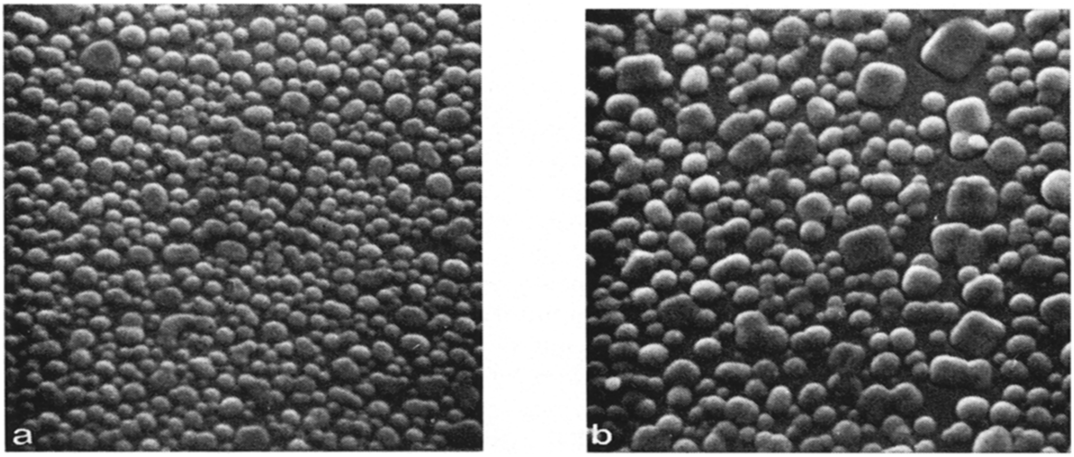


Fig. 6. NaCl particle growth in the course of time for the dynamic procedure. SEM pictures (10 × 10 μm) of an alkali-glass (B44) capillary at 350°. (a), 1 h; (b), 6 h.

during storage[38]. The alkaline water film thus formed attacks the vitreous silica network and the result is a loose layer of hydrated silicates. Attempts to etch such surfaces are bound to fail. As judged by the naked eye, NaCl is formed readily and the column turns opaque. SEM pictures, however, revealed that recrystallization did not occur in such columns or that it occurred to an unpredictable and non-uniform extent. Also, the formation of conglomerates of NaCl particles was frequently observed, which ultimately grew to particles of impractically large dimensions at the cost of smaller ones. The description of the normal etching process given above, holds fully only with pre-conditioned columns.

Surface roughening by controlled surface devitrification

Commercial soda-lime–silica glasses do not readily devitrify during heat treatment. The exchange of Na_2O for Li_2O promotes devitrification considerably, as near and above the softening point the mobility of Li^+ ions is large compared with that of the Na^+ ions[40,41]. The mere exchange of Na_2O with Li_2O, however, will not lead to an appreciable rate of crystallization during heat treatment, as the rate of homogeneous nucleation is very small. Stookey[42], in a study on controlled crystallization of lithium-rich glasses, used colloidal silver as a nucleation agent. Recently, Petzold and Kambor[43] described the introduction of silver in glass based on ion exchange between the glass and a mixture of molten nitrates, containing small amounts of $AgNO_3$. Ernsberger[44] reported that the exchange of Na^+ ions in glass with Li^+ ions from a mixture of $LiNO_3$, $NaNO_3$ and KNO_3 proceeds smoothly.

We chose to treat the glass with a mixture of molten nitrates, relatively rich in $LiNO_3$ and containing only small amounts of silver nitrate. Because of the considerably smaller size of the Li^+ ions (ratio of radii, Li^+:Na^+ = 0.63), replacement of Na^+ with Li^+ causes the glass surface layer to shrink. Under the experimental conditions used, micro-cracks form spontaneously. The melt penetrates into these cracks and the rate of penetration of Li^+ and Ag^+ into the glass is determined by the rate of propagation of the cracks, rather than by diffusion. The result is a cloudy surface layer of cracked ion-exchanged glass, the thickness of which is proportional to the time of ion exchange. Under the conditions used (see Experimental), the mean rate of propagation was 2.5 μm/min. The Ag^+ ions in the glass were readily reduced by treatment with hydrogen at elevated temperatures[43].

During drawing of the pre-treated tube, the following processes take place:

(1) growth of silver crystals to a minimum critical size for nucleation;

(2) nucleation of devitrification;

(3) growth of crystals in and on the surface;

(4) diffusion of Li^+ away from the surface in exchange for Na^+ from deeper layers;

(5) production of "new" surface as a consequence of the macroscopic surface increase during drawing;

(6) reduction of the "old" surface area as the cracks in the surface disappear at temperatures well above the softening point.

Maurer[45] studied the effect of catalyst size in heterogeneous nucleation and found that colloidal particles, smaller than 80 Å, were not effective as nuclei. Stookey[42] found that nucleation did not occur above a certain critical temperature. This temperature should not be attained before the Ag crystals reach the critical size for nuclea-

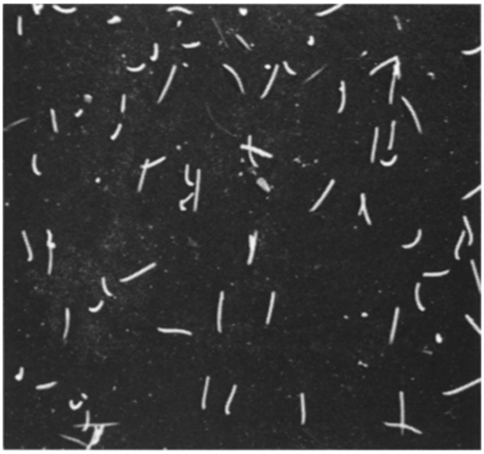


Fig. 7. SEM picture (50 × 50 μm) of an alkali glass (Rö 06) after controlled surface devitrification.

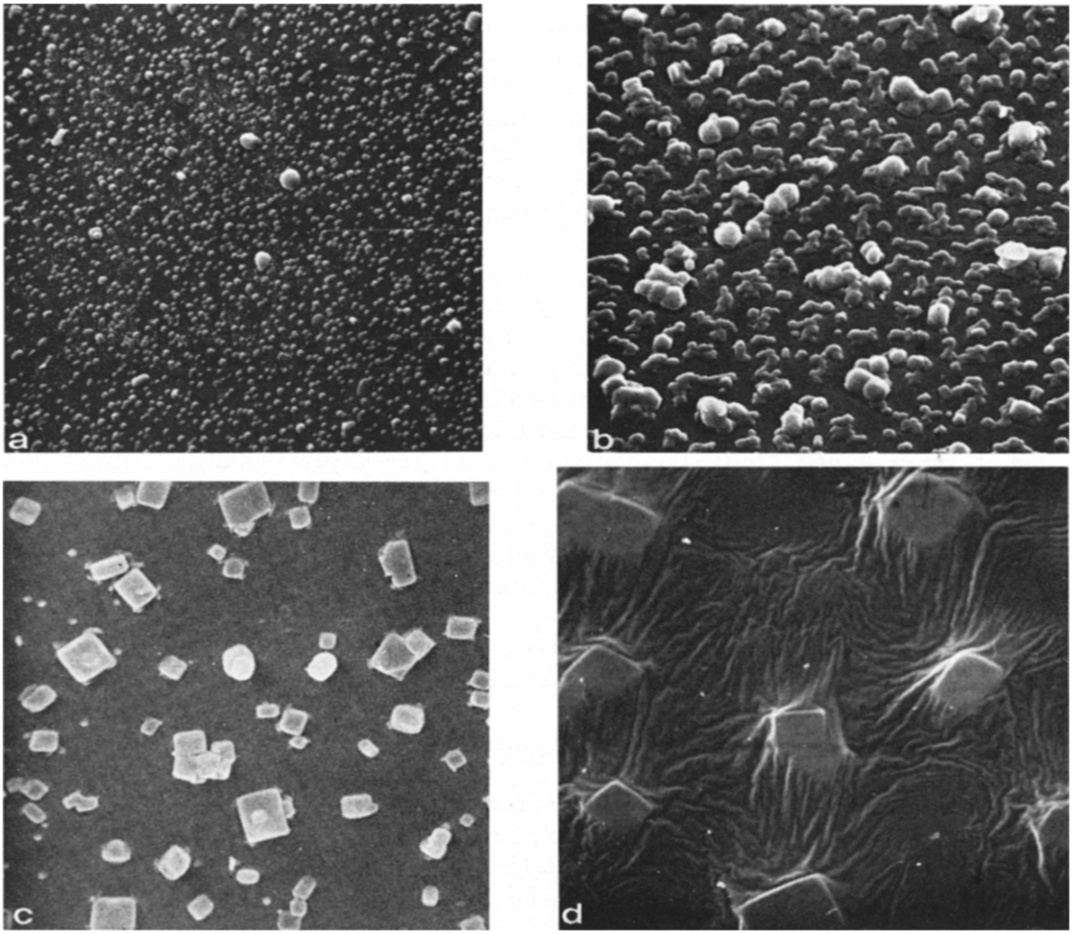


Fig. 8. SEM pictures (20 × 20 μm) of various stages in the preparation of an OV-225-coated NaCl SCOT column, I.D. 0.4 mm. (a), After one rinsing; (b), after 5 rinsings; (c), after recrystallization during 1 h; (d), after coating and use during 2 weeks at 225°.

tion, or crystallization of the glass will not occur. Therefore, the inner wall of the tube should not undergo too steep a temperature programme.

Although the nature of the crystals grown has not yet been established, the presence of lithium metasilicate or lithium disilicate is likely[41,42]. If Li^+ is incorporated in the crystal phase, steps 4 and 5 are competitive with step 3 and the net result depends on the coherence of the temperature programme that the tube undergoes, the temperature and time of pre-treatment and the elongation factor.

Under the particular set of conditions described (*cf.* Experimental), interesting "spiked" surfaces are obtained (Fig. 7). The dimensions of the spikes (diameter 0.3–0.5 μm, length 1–4 μm) compare reasonably well with stationary phase film thicknesses normally used. In a certain sense these surfaces can be compared with those reported by Schieke *et al.*[25]. In experiments in which the ion exchange was performed at 250° for 2 h instead of at 240°, the surface was uniformly covered with clusters of spikes, rather than with single spikes. The same experiments performed with A.R. glass instead of Rö glass did not yield predictable results.

As judged from the results of an intermediate test, according to Rutten and Luyten[46], these surfaces are well suited for gas chromatography. Current methods of deactivation proved fully satisfactory, which is in marked contrast to results obtained with columns that had merely undergone the ion exchange of Na^+ for Li^+ as was proposed by Desty[26]. These columns exhibited severe adsorption and catalytic activity, and could not be deactivated by current methods.

The final result of the surface devitrification depends on many parameters and the influence of each of these parameters is not yet fully understood. A better predictability of the length and closeness of the spikes will be the subject of further studies.

Deposition of NaCl particles on the column wall

Fig. 8 shows SEM pictures of coated and uncoated columns treated with an

TABLE II

COMPARISON OF THE PERFORMANCE OF OV-225-COATED COLUMNS AT 225° USING NITROGEN AS CARRIER GAS

SCOT = Support-coated open tubular.

Parameter	*Column No.*					
	1	*2*	*3*	*4*	*5*	*6*
Column type	SCOT*	SCOT*	SCOT*	HCl etched	HCl etched	SCOT
Support	Chromosorb R 6470-1	Cab-O-Sil	Cab-O-Sil	—	—	NaCl
Coating method	Dynamic	Dynamic	Dynamic	Static**	Static**	Static**
Length (m)	50	25	34	40	42	18.4
I.D. (mm)	0.4	0.4	0.4	0.25	0.25	0.35
Theoretical plates/m***	1780	1460	2340	2350	2480	2750
Coating efficiency (%)	63	52	82	52	56	86

* Prepared according to refs. 32 and 34.

** According to ref. 47.

*** Achieved at capacity ratios between 8 and 11.

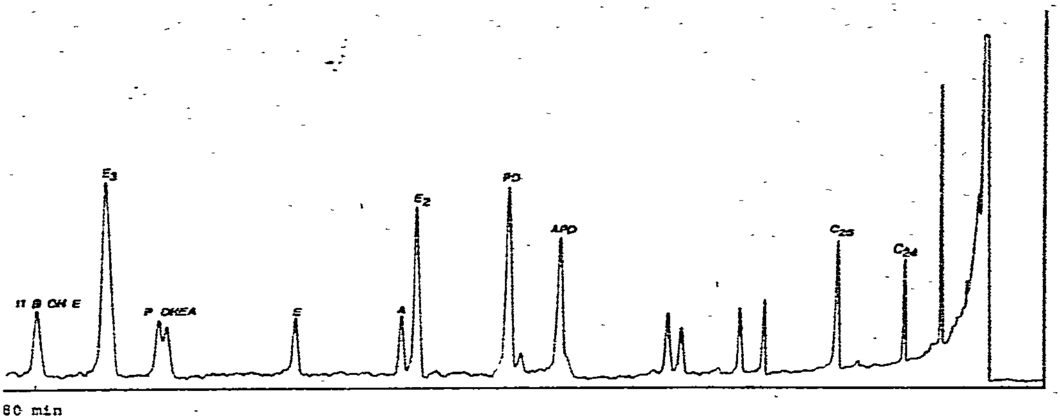


Fig. 9. Chromatogram of a mixture of trimethylsilyl derivatives of steroids on an HCl-etched glass (A.R.) capillary column (No. 5, Table II). APD = Allopregnanediol; PD = pregnanediol; E_2 = estradiol; A = androsterone; E = etiocholanolone; DHEA = dehydroepiandrosterone; P = pregnanolone, E_3 = estriol; 11-β-OH-E = 11β-hydroxyetiocholanolone.

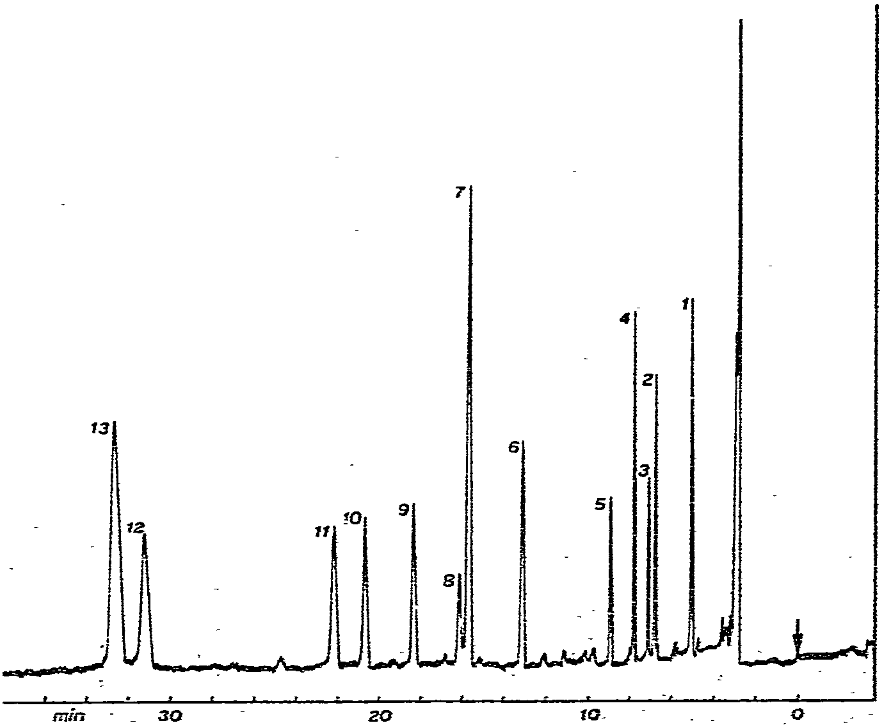


Fig. 10. Separation of a standard mixture of chlorinated pesticides on an NaCl SCOT column (No. 6, Table II). 1 = Hexachlorobenzene; 2 = 2,2′-dibromobiphenyl (internal standard); 3 = α-BHC; 4 = aldrin; 5 = γ-BHC; 6 = o,p′-DDE; 7 = p,p′-DDE; 8 = β-BHC; 9 = dieldrin; 10 = o,p′-DDT; 11 = o,p′-DDD; 12 = p,p′-DDT; 13 = p,p′-DDD.

NaCl sol. After one rinsing, the wall is uniformly covered with spherical particles, about 0.3 μm in diameter (Fig. 8a). Repeated rinsings increase the amount of NaCl and conglomerates of particles are seen (Fig. 8b), which, on heating, recrystallize within 1 h to cubic crystals of 0.5–2 μm (Fig. 8c). The rate of crystallization is considerably higher than for HCl-etched columns. This effect might be caused by minor impurities in the NaCl particles of the etched columns, possibly $CaCl_2$; isotachophoretic analysis revealed the presence of trace amounts of Ca^{2+}.

Performance of coated columns

Preliminary results of polar phase-coated columns, including some SCOT columns, are presented in Table II. Fig. 9 shows a chromatogram of a standard mixture of trimethylsilyl derivatives of steroids at the end of a period of 6 weeks at 225° (column 5). Fig. 10 shows a separation of chlorinated pesticides after 4 weeks of operation at 225° (column 6).

The stability of the columns 4–6 appears to be good. After decreasing about 10% during the first three weeks, the capacity ratio remained constant. Plate numbers and relative retentions remained constant within experimental error during the period studied (up to 6 weeks now). Adsorption effects and minimal sample quantity are well within the limits for reliable analysis, while bleeding and loading capacity enable coupling to the mass spectrometer.

CONCLUSION

The types of surface roughening reported here are in various stages of development.

For HCl-etched columns, we have shown that, under properly chosen conditions of pre-treatment, etching time and temperature, the size, shape and distribution of the particles can be predicted. This permits a systematic study of the relationship between these factors and column properties.

The preparation of NaCl SCOT columns is easy to carry out. The NaCl suspension will not clog narrow columns, which is an advantage over current supports. The direct deposition of NaCl particles yields a roughening of the column wall which is an attractive alternative for the HCl etching and is applicable to any type of glass.

The thermal stability of OV-225 columns appears to be very good.

The development of the method of surface devitrification is still continuing. We regard the results obtained so far an incentive for further work. The dimensions and shapes of the observed spikes and the easy deactivation of the column add to this optimism. In particular, the closeness and length of the spikes deserve further optimization.

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